# METHOD FOR TREATING A SEMICONDUCTOR MATERIAL FOR SUBSEQUENT BONDING

## BACKGROUND ART

The invention generally relates to the treatment of materials, and in particular for treating a semiconductor material for subsequent bonding. The technique includes bombarding a surface of the semiconductor material with a beam containing a controlled number of ions in ion clusters. The beam etches a pattern in the surface, and the number of ions is controlled to provide a desired roughness of the surface pattern to improve adhesion during subsequent bonding . The invention may be applied to substrates for use in electronics, optics and optoelectronics.

Processes for manufacturing detachable substrates are known. Such processes use two layers of material, for example semiconductor materials such as silicon, to fabricate "detachable" substrates. The expression "detachable" substrate means a substrate that comprises two layers that have been bonded together, wherein the bonding is reversible so that it is possible to separate the two layers along their bonding interface. Detachable substrates thus include two layers integrally attached at a bonding interface. The cohesion energy between the two layers is controlled so that it is sufficiently great to guarantee good cohesion of the two layers forming the detachable substrate, even when the substrate is subject to thermal and/or mechanical treatments (for example, thermal treatments such as high temperature annealing, and mechanical treatments such as polishing the substrate surface). The cohesion energy is also sufficiently small so that the layers can be separated at a weakened zone formed between the two layers if desired (for example after the substrate has been subject to certain treatments). Typically the two layers of the detachable substrate are detached via a mechanical action, for example by use of an object such as a blade.

The term "bonding" in the context of the treatment of very thin layers means to put two layers into contact to create links, via molecular adhesion, between the bonded surfaces of the two layers. These links may typically be hydrogen links, and their development can be stimulated by pre-treating the layers that are to be bonded.

Pre-treatments applied prior to bonding can, for example, include a cleaning stage that consists of dipping the layers successively in an alkaline bath and then in

an acid bath. The layers are dipped in an alkaline bath to develop the hydrophilic properties of the layers, by creating OH type links on the surface of the layers. The acid bath eliminates any contaminating elements (in particular metals) from the surface of the layers that may have been generated during previous treatments of the layers (and in particular the alkaline bath). Pre-treatment can also involve exposing the layers to a plasma, for example, or may include other known techniques.

The surface condition of the layers to be bonded is subject to very strict specifications, especially when the layers are to be used to manufacture substrates for electronics, optics or optoelectronics applications. It is thus common to have to meet roughness specifications which must not exceed a few Angstroms in rms value (root mean square).

Roughness is generally measured with an AFM (Atomic Force Microscope). This equipment can measure the roughness on a scanned surface by using the tip of the AFM, ranging from $1\times1\ \mu m^2$ to $10\times10\ \mu m^2$, and in rare cases from $50\times50\ \mu m^2$, or even $100\times100\ \mu m^2$. Since the surface condition of these layers are generally very smooth, bonding s accomplished by simply contacting the surfaces of the two layers together. In some cases, such bonding may be complemented by compressing the structure made of the two layers.

It is known to make detachable substrates by applying a surface condition adjustment treatment to the surface of at least one of the two layers to be bonded. Such a surface condition adjustment treatment consists of applying a "wet" etching treatment to the surface, which means using a liquid to attack the surface to adjust its roughness. For example, the surface to be treated may be an oxide, and the liquid may be hydrofluoric acid. The surface oxide may be in particular a silicon dioxide. Attacking the surface with a liquid permits one to modify the surface as desired, such as to increase its roughness to a desired level. For example, to modify the surface so that it can bond with another layer, but also allow for separation of the bond later via a mechanical action. The desired roughness (typically a roughness of about 5 Angstroms rms to make a detachable substrate) is achieved by controlling the length of time the surface is exposed to the liquid.

Thus, one of the known techniques to make detachable substrates involves attacking the surface of at least one layer with a liquid, in order to increase the roughness of this surface. An inconvenience of such methods is that some parts of the layer that should not be attacked may happen to be exposed to the liquid. Consequently, when only one side of a layer should be treated, the opposite side of the layer may happen to be attacked considerably by the liquid.

It is possible to protect certain parts of the layer during wet etching. For example, the parts could be covered with a protective element, for example a varnish. But this implies the use of specific and complex equipment. Moreover, such protective means do not necessarily make it possible to systematically prevent the liquid from attacking certain other parts (notably the lateral parts of the layer). In addition, implementing such protective means may require additional handling of the layers, and thus additional risks of damaging these layers (which may be extremely fragile, particularly in the case of thin layers as mentioned above).

Moreover, if the purpose is to control the spatial distribution of side regions of a layer whose roughness is to be adjusted via the known technique of wet etching, it is necessary to plan for relatively heavy and complex means and a complicated protocol in order to only etch the desired side regions. It is necessary to cover the side of the layer with a mask to form a spatial pattern which allows access to only the regions which are to be etched (positive mask), or prevents access to only regions which are to be protected from etching (negative mask). The layer to be etched and its mask are exposed to wet etching. It is then necessary to remove the mask. This is achieved via chemical products and/or via exposure to a plasma. Such means to remove the mask are likely to damage the surface of the layer, and/or leave some contaminating elements on the surface. These contaminating elements can in particular be hydrocarbons issued from the resin that formed the mask. The hydrocarbons then are an obstacle to bonding the layer via molecular adhesion. Consequently, manufacturing a detachable substrate from such a layer is difficult.

Thus, it appears that known solutions for making detachable substrates have limitations.

SUMMARY OF THE INVENTION

The invention relates to a method for treating a semiconductor material for subsequent bonding. The technique includes bombarding a surface of the semiconductor material with a beam containing a controlled number of ions in ion clusters. The beam etches a pattern in the surface, and the number of ions is controlled to provide a desired roughness of the surface pattern to improve adhesion during subsequent bonding.

In an advantageous embodiment, the method also includes bonding the surface layer of the semiconductor material to a second surface of a semiconductor substrate to form a detachable substrate structure. In a preferred implementation, the ions are of a chemically inert species in relation to the semiconductor material, and the semiconductor material may be made of at least one of silicon or silicon carbide, and the ions may be argon ions or nitrogen ions. In a variation, the surface is bombarded with ions that are capable of chemically reacting with the semiconductor material, and the ions may be generated from a plasma. When the ions are capable of reacting with the semiconductor material, the surface layer and the plasma may respectively be of Si and $SF_6$, SiC and $SF_6/O_2$, $SiO_2$ and $SF_6/O_2$, $SiO_2$ and $CHF_3/SF_6$, $Si_3N_4$ and $CHF_3/O_2/SF_6$.

In a beneficial implementation according to the invention, the number of ion clusters is controlled to smooth the surface to a roughness value suitable for molecular bonding. The number of ions may be controlled by controlling the pressure of an ion source that generates ion clusters. In addition, an acceleration voltage that is applied to the beam may be controlled to control the speed of the ion clusters which influences the etching of the surface. In a preferred embodiment the ion clusters are directed to selectively treat desired zones of the surface to create an adjusted pattern.

In another advantageous embodiment, the invention includes focusing the beam such that the ions, monomer species of the ions, and the ion clusters are directed towards the surface of the semiconductor material. Moreover, the beam of ion clusters may be directed to a selected impact site on the surface of the semiconductor material, and the semiconductor material may be moved to provide the desired pattern. An appropriate spatial pattern can thus be created on the surface

layer having a different roughness in comparison to other portions of the surface. Furthermore, a plurality of patterns with variable roughness can be created on the surface.

Advantageously, according to the invention, the semiconductor material is one that is recycled after removal of a transfer layer. In addition, the semiconductor material may include at least one layer of a material that is different than the semiconductor material, with the outer surface of the layer being etched by the bombarding. Preferably, at least two layers of materials that are different than the semiconductor material can be provided, such as a buried layer and an insulating layer, with the outermost layer being the surface that is etched prior to bonding.

The present invention thus overcomes the limitations of the prior art, and further allows for precisely controlling the surface condition (and in particular the roughness) of a layer of semiconductor material that will be used to assemble a detachable substrate. In particular, the present invention permits fine adjustments of the roughness of the surface, and permits the selection of either increasing or reducing the roughness of the surface. Moreover, the invention permits local adjustments to be made to the surface of semiconductor material, and the adjustments can be made according to a predetermined spatial pattern, without being subject to the inconveniences associated with conventional treatment methods.

BRIEF DESCRIPTION OF THE DRAWINGS

Other aspects, purposes and advantages of the invention will become clear after reading the following detailed description with reference to the attached drawings, in which:

Figure 1 is a schematic diagram of an installation for bombarding a wafer with ion clusters according to the invention;

Figures 2a and 2b are graphs that represent the evolution of the roughness of a surface that has been bombarded with ion clusters, under different conditions according to the invention;

Figure 3 is a histogram illustrating the influence of pressure upon ion generation, in particular the creation of ion clusters.

Figures 4a to 4c illustrate a particular implementation of the invention, in which a surface is selectively and locally treated to adjust its surface condition according to a desired pattern.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 1 illustrates an implementation of an installation 10 for bombarding a layer 20 of material with a beam 30 of ion clusters. The word "ions" may designate ions that are "pure", but also may designate species created from several ions and which are electrically charged. Generally speaking, the "clusters" as used herein, are globally ionized, meaning that they have an electric charge other than 0. But these clusters can further include ions of other species, including molecules.

The layer 20 is of a semiconductor material. As will be explained below, it can either be silicon or silicon carbide, or another semiconductor material (SiO2 or Si3N4, for example).

The installation 10 comprises a source 101 of pressurized gas, capable of generating a parallel beam of gas ion clusters from a plasma internal to the source 101. The gas used can for example be argon or nitrogen. The control of the characteristics of the plasma allows for defining the configuration of the ion clusters. In particular, the pressure of the plasma source 101 is controlled in order to control the average number of ions present in the clusters, as will be explained in detail below with regard to Figure 3. In addition, control of the acceleration voltage allows for controlling the speed of these clusters.

The layer 20 is a layer whose surface conditions are to be modified in a controlled manner so that it can be assembled, via bonding, with another layer (whose surface condition may also have been adjusted) to create a detachable substrate.

According to a first alternate implementation, ion clusters such as those described above are projected onto the surface of the layer 20, and this bombardment includes no chemical reactions. In this case the bombardment is thus purely "ballistic", because the ion clusters are chemically inert in relation to the material of the layer 20. In such a case, the bombarded clusters are typically made of argon or nitrogen.

According to another alternative implementation, ion clusters of a particular species capable of chemically reacting with the material of the layer 20 could be used. In this case the bombardment is said to be reactive, and the bombarded ions can be made of oxygen or an oxygen compound.

In the case of a reactive bombardment of ions, it is also possible to further utilize an etching plasma (that is different from the plasma of the source 101) in a zone of the device 10 through which the ion beam will need to pass, and which is located in the region of the device 10 that is immediately upstream from the layer 20. In the particular embodiment including an etching plasma, it can for example be planned that the material of the surface of the layer 20 and the plasma element consist of one of the following pairs: (Si, $SF_6$), (SiC, $SF_6/O_2$), ($SiO_2$, $SF_6/O_2$), ($SiO_2$, $CHF_3/SF_6$), ($Si_3N_4$, $CHF_3/O_2/SF_6$). In this case, the ion clusters created by the source 101 chemically react with the etching plasma. In addition, the etching plasma itself can also chemically react with the surface of the layer, as well as the species having passed through the etching plasma with the layer.

Referring again to Figure 1, the installation 10 shows that the ion beam is generated by the source 101 and then passes through an accelerating chamber 102. The chamber 102 accelerates the ions clusters of the beam from the source 101 to a desired velocity, thanks to an acceleration electric voltage which can be controlled. In this text the "acceleration voltage" of the source 101 actually corresponds to the acceleration voltage of the accelerating chamber 102.

The beam then passes through a beam-creating electromagnetic structure 103. This structure 103 allows adjustments to the characteristics of the magnetic field of the beam (i.e. to collimate or focus the beam), via the application of electromagnetic fields with desired characteristics. The beam then passes through a magnetic annular structure 104 which also allows for the creation of a field with controlled characteristics, in order to selectively deviate the charged species of the ion beam. The beam issued from the accelerating chamber 102 and the electromagnetic structure 103 comprises ion clusters of the bombarded species, but also molecules which are electrically neutral (in particular monomers of the bombarded species). The trajectory of the different elements of the beam is represented in Figure 1as being rectilinear. However, in reality these trajectories are not rectilinear, and the

radius of curvature of the trajectory depends on the mass of the ions and of the different elements of the beam. By precisely controlling the characteristics of the magnetic field generated by the magnetic annular structure 104, it is possible to selectively deviate only the desired ion clusters towards the opening of a screen 106. The other constituents of the beam do not pass through this opening because they are stopped by the screen 106.

In a variation, the structure 103 and the structure 104 can be one and the same. In addition, an electrical neutralizing structure 105 may also be provided.

A screen 106 with an opening 1060 is positioned to let pass only the part of the beam that comprises the desired clusters, so that the desired ion clusters can have an impact on the layer 20 located behind the opening 1060. The screen 106 and its opening 1060 may be fixed parts of the device. The portion of the beam that passes through the opening to impact the layer 20 corresponds to a focalized beam, after the beam passes through of the means 103. Therefore, the layer 20 is impacted by the beam of ion clusters over a basic surface of very small dimensions (the section of the beam that passes through the opening 1060 has a width of about one or possibly only about a few millimeters). The layer 20 in this implementation is mounted on a movable support 107, which can be controlled to displace the layer 20 in the plane perpendicular to the beam, for example.

It is thus possible to precisely define an etching pattern of the ion clusters on the surface of the layer 20, by displacing the layer according to a desired trajectory using the moveable support 107. In this manner, the impact site of the ion clusters on the layer 20 traces a special pattern. This aspect will be further considered later.

Again referring to Figure 1, the installation 10 also includes a screened room 108 located behind the layer 20 and the displacement means 107, which faces the impact zone of the beam on the layer 20. This screened room 108 is connected to a device 109 capable of determining the dose of species received by the layer 20.

The bombardment of the layer 20 with ion clusters of desired characteristics thus allows for adjusting the roughness of the surface, with the aim of making a detachable substrate. It is to be noted that, in comparison with known techniques to modify the surface conditions via wet etching, the bombardment with ion clusters avoids the inconveniences described above. In particular, no "leak" or contamination

can occur because the present technique modifies the surface roughness by using a "dry" etching technique, and not a "wet" etching method. Thus, the layer 20 does not come into contact with liquids.

Moreover, the present installation and method permits very precise control of the impact zone to be bombarded on the surface with the ion clusters. This is also true for the situation wherein the layer is not displaced, as the dimensions of the section of the beam that impact the layer are very small, as already mentioned. Further, the fact that the bombardment occurs not simply with ions but with clusters of ions, allows for great freedom to adjust the surface roughness of the layer 20. In particular, it is possible to selectively reduce, or increase, the surface roughness of the layer 20.

It has been observed that, depending on the characteristics of the bombardment with ion clusters, it is possible to either increase or reduce the roughness. In particular, with reference to Figure 2a, schematically represented are several curves C1 to C5 that are substantially rectilinear. These curves translate the evolution of the roughness R of the surface of the layer 20, versus the evolution of the voltage V applied to the beam inside the accelerating chamber 102. Each of the curves in Figure 2a corresponds to a bombardment condition in which the ion clusters mainly comprise a respective number of ions. The control of the bombardment parameters allows a determination of the number of ions present in the clusters that bombard the layer 20. The main parameter that controls the number of ions present in the clusters is the pressure inside the ion source 101. Thus, the pressure of the source 101 can be controlled to control the number of ions in the clusters. This is illustrated on the histogram in Figure 3.

Figure 3 shows several curves A1, A2, A3, A4. Each of these curves represents the size repartition of the ion clusters, for a given source pressure. The size of the clusters is represented by the number of atoms per cluster (upper horizontal scale), which here varies from 0 to 3000 atoms per cluster. The lower curve A1 is associated with a pressure of 760 Torr, the curve A2 with a pressure of 2300 Torr, the curve A3 with a pressure of 3000 Torr, and the curve A4 with a pressure of 3800 Torr. The peak of these curves. which corresponds to the most common cluster size for the pressure in question, has greater values as the pressure

increases. This histogram was taken form the article entitled: "Materials processing by gas cluster ion beams", Material Science and Engineering, R34, N°6, p244 (2001). Thus, as shown, the number of ions present in each cluster lies around an average number "N" of ions per cluster. It is thus possible to control the value of N by controlling the pressure of the ion source.

Each curve in figure 2a thus corresponds to a different value of N. The value of N increases when the curve changes from C1 to C2, to C3, to C4, and to C5. The curve C1 corresponds to a bombardment with individual ions, which means that N equals 1. Under these conditions, as the acceleration voltage of the ions of the beam increases, the surface roughness of the layer 20 subject to bombardment of "clusters", each made of a single ion, increases considerably. In this situation, the ions individually bombard the layer and cause major damage to the surface structure of the layer.

The curve C2, immediately below the first curve, corresponds to bombardment conditions under which N has a value greater than 1. In this case the same increase in acceleration voltage does not result in as great an increase of the surface roughness, even though the roughness does increase. The next curve C3 illustrates a low increase of roughness for the same increase in the voltage V. Lastly, the curve C4 corresponds to bombardment conditions under which the bombarded clusters comprise a rather large number of ions, and it illustrates a constant roughness despite the increase in the acceleration voltage V.

Thus, when the ion clusters comprise a number N of ions greater than a given threshold, the slope of the resulting curves Rf(V) approaches zero, under certain conditions. This threshold depends on the starting surface condition of the layer, prior to bombardment. Moreover, when the number N continues to increase, bombardment does not increase the surface roughness of the layer 20, but rather reduces it by smoothing this surface. This situation is illustrated by the curve C5.

By adjusting bombardment conditions, and more precisely the number of ions present in the clusters, it is possible to adjust the surface condition of the layer 20 in a desired manner by increasing to a greater or lesser extent the surface roughness of this layer, or even by reducing the roughness. This is useful in cases where the surface of the layer 20 has a high roughness before bombardment.

Consequently, two parameters define bombardment conditions that have a major influence on the progression of the process. First, the pressure associated with generating ions allows one to control the number of ions present in the clusters. Second, the acceleration voltage allows one to control the speed of the clusters, and also has an influence as described with reference to Figures 2a and 2b. This influence can be exploited by programming bombardment sequences during which different regions of the layer 20 are subject to cluster bombardments of different numbers of ions, to selectively adjust the surface roughness of the different regions in a desired manner. For this purpose, the means of displacement 107may advantageously be programmed to displace the layer 20 in conjunction with changes to the parameters to modify the value of N during different successive stages of a given bombardment process of the layer.

Figure 2b represents the evolving surface roughness R of the layer 20 subject to bombardment with ion clusters that includes an average number N of ions which can vary (here again corresponding to different curves in this figure), versus the acceleration voltage V. This Figure includes the curves C1 to C5 of Figure 2a. However, Figure 2b also shows another set of curves C'1 to C'5, which progress according to the same general logic as the curves C1 to C5 (increase in the number N from curve C'1 to curve C'5, for the same starting layer 20 and the same bombarded ions).

The curves C'1 to C'5 show that, contrary to the curves C1 to C5, an increase in the number N does not result in a reduction of the surface roughness of the layer 20. The curve C'5 corresponds to a number N that is very large, which can be associated with a value of N that approaches infinity. It should be noted that when the surface condition of the layer 20 already corresponds to a low roughness (curves C'1 to C'5), it is impossible to further smooth the surface by increasing N. Thus, starting with a layer whose surface is relatively rough, it is possible to selectively increase, or reduce, the roughness.

An interesting application of the present method is when a surface layer 20 of a wafer has surface conditions that are incompatible with bonding via molecular adhesion (roughness greater than a value of about 5 Angstroms rms). The present invention can be used to advantageously treat certain regions of these wafers to

smooth them and bring these regions to a roughness value that enables such bonding. In particular, this allows for the recycling of donor wafers resulting from use of a layer transfer process such as the SMART-CUT® type process, by reusing them. In this case, it is possible to use layers made from a wafer whose intrinsic surface condition is incompatible with bonding (for example, SiC, III-V). Instead of proceeding to completely polish such a wafer, a bombardment with clusters comprising a rather large number N of ions makes it possible to smooth the surface of the wafer.

Moreover, the smoothing process can be precisely controlled, both in terms of the final roughness and in terms of creating a spatial pattern having more or less smooth regions with the aim of using the surface for bonding. However, if the starting surface condition of the layer 20 is inferior (less than a given threshold $R_0$), which depends among other things on the nature of the material of the layer and of the bombarded species, it will only be possible to increase the roughness. Thus, if the starting point of the curves C'1 to C'5 happened to be below the threshold $R_0$ (whereas it is situated at the level of this threshold in Figure 2b), it would not even be possible to retain this starting low roughness by proceeding with a bombardment of the surface. In particular, even a bombardment with a very great value of N would result in an increase of the roughness.

Figures 4a to 4c represent layers 20 that have been subject to a bombardment with ion clusters such as that described above, during which the roughness of certain regions of the surface of the layer have been selectively modified. Figure 4a shows a ring on the surface which has been created to have a roughness value lower than that of the rest of the surface, so that mechanical stability can be obtained on this ring when at the time of assembling the layer 20 with another layer (which may be homogeneously smooth, for example).

The displacement device 107 may be programmed to create any other desired pattern on the surface. Figures 4b and 4c thus respectively represent a layer 20 with a grid pattern, and with a paved pattern, each having a roughness lower than that of the rest of the surface of the layer. Further, by controlling the number N of ions in the bombarded clusters in conjunction with the displacement of the layer 20, it is thus possible to create any pattern, including one with several levels of roughness

selectively distributed over different desired regions of the surface. It is then possible to create patterns with variable roughness, to make detachable substrates having a controlled distribution of roughness over the surface. The expression “pattern with variable roughness” designates a pattern wherein different zones may have different roughness values.

It is to be noted that the present technique allows for the very fine control of the levels and distributions of roughness on the surface of a layer from which a detachable substrate is to be created, after conducting a reversible bonding process via molecular adhesion with another layer (whose roughness may have been adjusted if necessary).

It is also noted that proceeding with a bombardment with ion clusters only modifies the surface of the layer 20, no subsurface damage occurs by using such a bombardment process. In this regard reference can be made to the article “Substrate smoothing using gas cluster ion beam processing” by Allen and al., Journal of Electronic Materials, Vol.30, N°7, 2001.